



BIOREMEDIATION OF METALLIC IONS FROM AQUEOUS SOLUTION

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ABSTRACT

Use of *Moringa oleifera* seed pods (MSP) and *Arachis hypogea* nut shells (ANS) as a bio-remedial approach for removal of selected metals (copper, zinc, lead, cadmium, and iron) from synthetic contaminated water was investigated. Batch experiments were used for the bio-sorption of the metal ions. Removal parameters such as contact time, particle size, sorbent dose, and initial metal concentration were optimized. Determination of residual metal ions after employing sorbent was done using flame atomic absorption spectroscopy (FAAS). The removal efficiency of the two materials is compared. Using 20 ppm synthetic metal ion mixture in 50mL of water sample, the optimized parameters for *Moringa* seed pods were 150 min contact time for Cd and Cu while 100 minutes for Pb and Fe, 2.0 g of sorbent dose (except Fe which had its highest removal using 0.5 g sorbent). While using *Arachis* nutshells, the optimized conditions were 150 min for Pb, Cd and Fe, while 100 minutes for Cu and 2.0 g of sorbent dose. The decrease in removal with increasing particle size was observed for both ANS and MSP. Similar result was observed for both the sorbents as the initial metal concentration was increased, the removal efficiency was increased and after saturation, percentage removal is constant. Removal of Pb by both the sorbents was highest followed by Cd, Cu, Zn and Fe. These non-edible plant parts for *Arachis* and *Moringa* plants are proposed as a cheap, simple, and an effective alternative for purification of water contaminated with heavy metals.

KEY WORDS: *Arachis hypogea*, *Moringa oleracea*, bio-sorbent, metal ions, contact time, particle size, sorbent dose

INTRODUCTION:

Over the years, anthropogenic activities have greatly increased the level of toxic metals, especially in aqueous systems therefore, efficient and cost effective methods are being sought for their removal. Conventional physical and chemical methods of metal removal from aqueous streams that have been applied include chemical precipitation, ion exchange, adsorption and electrochemical techniques, (Reed and Nonavinakere, 1992; Atwood et al., 2002). These methods, which are plagued with incomplete removal, involve the use of large volume of chemicals, high cost especially when contaminant concentrations are within the ranges of 10-100mgL⁻¹. They are laborious and generate other wastes that require further disposal (Rostami and Joodaki, 2002). Advances towards effective treatment methods for the removal of heavy metals in aqueous media involve the use of micro-organisms (Viraraghavan and Yan, 2003; Ma et. al., 2004) have been reported. Attention was also focused on the application of fungal species for metal removal from aqueous media using either the batch or continuous modes (Awofolu et al., 2006). Lately, the use of waste materials from plant origin and other agro wastes as sorbents of toxic metals from aqueous medium is gaining attention due to their ability to absorb toxic metals from aqueous systems. This is also because agro-wastes are readily available, cheap, biodegradable, sludge free and involve small initial cost and land investment (Uppendra 2006; Horsfall, et. al., 2003). Researches into their applications are becoming popular instead of physical and chemical methods, which are plagued, with several problems and disadvantages as mentioned above. Several plant based materials have been explored and reported in this regard. Cassava tuber back wastes (CTBW) was investigated (Horsfall et. al., 2003). *Alfalfa*, *Medicago saliva* (Gardea-Torresdey, et al., 1996) and *Moringa oleifera* seeds.

MATERIAL AND METHODS:

All the standard solutions were prepared from analytical grade compounds of Merck Company. All the glassware used was of Borosil. Prior to all chemical analyses, the reagent bottles, conical flasks, beakers, sample bottles and volumetric flasks were cleaned by soaking overnight in 2N hydrochloric acid, rinsed with water and oven dried at 60°C. Orbital shaker (Scigenics), agate pestle, and mortar were also used for reducing the particles further. 1mm, 2mm, and 4mm stainless steel sieves were used for sieving the sorbents. The filter papers used were ash less Whatman filter paper number 1 from England. Working solutions were prepared from the stock standard solutions (1000 mg/L) of the metals lead, cadmium, copper, iron and zinc.

Preparation of MSP and MNS: The two plant material i.e. fruits of *Moringa oleifera* and *Arachis hypogea* (approximately 1 kg) were procured from the local vegetable market of Raipur. Both the samples were deseeded and were thoroughly washed in de-ionized water to remove dirt particles contained in them. The samples were then air dried in shade at room temperature for three (3) days. The plant waste material of *Arachis* nut shells (ANS) were further dried in the oven at 60°C for 04 hours while the *Moringa* seed pod (MSP) was allowed to dry at the same room temperature for 42 hours in order to blend them into a powdery form in a food blender. The powder was then sieved using 1mm sieve and kept in an air tight sealed plastic/ glass container which was kept in desiccators in order

to preserve it from humidity. To avoid sample contamination, all handling and preparation steps were carried out on clean benches.

Determination of Metal Concentration in Sorbent Material: Both the adsorbents were digested with standard nitric acid digestion method. Filtrates were then transferred into separate plastic bottles, labeled and diluted appropriately and stored at 4°C. Initial metal concentration was determined with AAS. Table 1 reflects the concentration of the selected metals.

Bio-sorption of Heavy Metal Ions: Batch experiments were used for the bio-sorption of Cd, Cu, Fe, Zn, and Pb. Stock solutions at various concentrations were prepared from 1000mgL⁻¹ of each metal standard. Solution of known metal ion concentration was prepared and known amount of sorbent (MSP or MNS) was added. The mixture was shaken with a controlled orbital shaker and the concentrations of the unadsorbed metal ions in solutions were determined after separation of the sorbent by filtration using Whatman paper number 1 filter papers. The effects of contact time (0– 240min), initial metal concentration (1–20mgL⁻¹), sorbent dose (0.5–2.5 g, in 50mL–1) and particle size (1, 2 and 4 mm) were studied. Analysis and instrumentation were done using FAAS with air/acetylene. The amount of the metal adsorbed (% removal) by the sorbent was calculated using:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100,$$

Where C_i is the initial concentration before adsorption and C_f is the concentration after adsorption of metal ions. All experiments were done in replicates and reported as the average of the experiments.

RESULT AND DISCUSSION:

Effect of Contact Time: It was observed that when ANS sorbent was used for metal removal, the highest removal of Pb, Cd and Fe was reached within 150 minutes (Figure 1) while Cu within 100 minutes, the equilibrium was reached and further increase in time did not show any significant change. Percentage removal of the metal ions with the MSP increases with increase in contact time (Figure 2). More time allows the adsorbent particle to interact with the metal ion and increase chances of more adsorption (Jimoh, 2012). The highest removal of Cd and Cu was reached within 150 minutes while maximum removal of Pb and Fe was observed at 100 minutes. Highest removal of Zn was observed at 50 minutes with both the adsorbents.

Effect of Particle Size: The smaller the particle size the higher the surface area per unit weight of sorbent and hence higher percentage removal is expected (Bhatti et al, 2007) and this decrease in removal with increasing particle size was observed for ANS and MSP. As shown in Figures 3 & 4 the percentage removal of the metal was effective at sorbent particles size 1mm as compared to larger particles (2 mm & 4 mm). Similar trends have been observed by other researchers (Amuda et al., 2007, Nadeem et al, 2006). The ionic sizes trend of the metals is Pb > Cd > Zn > Cu > Fe for divalent cations. The larger ions are

expected to be removed first and the order of removal should decrease from Pb to Fe (Lee, 2008) but in some case it will be different depending on the environment of the interacting sites. This trend was not observed completely and this could be attributed to the fact that the metals were interacting differently with the ANS and MSP adsorbing sites. The present research showed the following order of metal removal efficiency $Zn > Cd > Cu > Pb > Fe$ with ANS and $Cu > Cd > Fe > Zn > Pb$ with MSP.

Effect of Sorbent Dose: It is expected that, as the sorbent amount increases, the number of sorbent particles surrounding the metal ion or ratio of sorbent particle to metal ion increases (Iftikhar et al., 2009). This increases the surface area on which the metal ions bind to the surface of the sorbents, hence increasing the removal efficiency. However, a further increase beyond the optimum sorbent dose decreases the percentage removal and this is attributed to the fact that there is possibility of the particles overlapping and overcrowding resulting in a reduction of the total adsorbent surface area and hence decreases the percentage removal (Rahman and Islam, 2009). Figure 6 shows that as the sorbent dose were increased from 0.5 g to 2.0 g of MSP sorbent, the percentage removal of metal ions increased and the optimum sorbent dose for the removal of Cd, Pb, Zn and Cu was 2 g except Fe which had its highest removal using 0.5 g sorbent. The results for metal removal using ANS adsorbent at different dosing levels (0.5 g to 2.0 g) showed a slight increase for cadmium, and zinc up to 2 g dosing level

(Figure 5), but no significant difference was observed for copper, lead, and iron at all dosing levels. Similar studies have been reported with other low cost sorbents (Khan and Wahab, 2007 Allen and Brown, 1995).

Effect of Initial Metal Concentration: As the initial metal concentration is increased, the removal efficiency is increased and after saturation, percentage removal is constant as shown in Figure 7, while using ANS. This could also be attributed to the saturation of the binding sites as more ions are added in the solution. As the concentration of metal ion increases, the number of metal ions competing for available binding sites on the sorbent increases. Therefore, binding sites become quickly saturated as the biomass amount remained constant (Rahman, 2009, Sharma et al. 2006). The same was observed using MSP; at lower concentration there was an increase in removal efficiency; however, after a threshold (different for each metal) any further increase in the metal concentration resulted in reduced removal efficiency for Pb, Cu, Cd, Fe and Zn (Figure 8). Removal of Pb by both the sorbents was highest followed by Cd, Cu, Zn and Fe. The minimum removal was observed for Fe and this was attributed to limited loading capacity of the sorbents due to saturation of iron binding sites. However increase in concentration decreases the removal of iron ions but low in comparison to the removal by other metals. This is because the concentration of residual iron ions in the sorbent was higher (Table 1) in comparison to the other metals.

Table 1: Heavy metal concentrations (mg/Kg) in Arachis Nut Shells (ANS) and Moringa Seed Pods (MSP)

Sample	Concentration of metals (mg/Kg)				
	Pb	Cd	Cu	Fe	Zn
ANS	0.37 ± 0.1	0.006 ± 0.001	0.075 ± 0.02	0.393 ± 0.04	0.19 ± 0.02
MSP	0.37 ± 0.02	0.008 ± 0.003	0.041 ± 0.01	3.865 ± 0.10	0.396 ± 0.03

Table 2: Heavy metal concentrations after different contact times with ANS as adsorbent

Initial metal concentration 20 (mg/L)	Final metal concentration (mg/L)							
	Residual conc. after 50 min	%Removal after 50 min	Residual conc. after 100 min	%Removal	150 min	%Removal	Residual conc. after 200 min	%Removal
Pb	4.26 ± 0.7	78.7	2.20 ±	89.0	2.03 ± 0.3	89.8	5.98 ± 0.5	70.1
Cd	4.30 ± 0.1	78.5	3.840 ± 0.3	80.8	3.800 ± 0.2	81.0	4.607 ± 0.2	77.0
Cu	4.394 ± 0.9	78.0	4.274 ± 0.7	78.6	4.400 ± 0.7	78.0	4.45 ± 0.7	77.7
Fe	5.91 ± 0.3	70.4	5.50 ± 0.2	72.0	4.9 ± 0.4	75.5	6.5 ± 0.2	67.5
Zn	4.80 ± 0.1	76.0	4.80 ± 0.1	76.0	4.91 ± 0.1	75.4	5.06 ± 0.1	74.7

ANS - Arachis Nut Shells

MSP - Moringa Seed Pods

Table 3: Heavy metal concentrations after different contact time treatment with MSP as adsorbent

Initial metal concentration 20 (mg/L)	Final metal concentration (mg/L)							
	Residual conc. after 50 min	%Removal	Residual conc. after 100 min	%Removal	Residual conc. after 150 min	%Removal	Residual conc. after 200 min	%Removal
Pb	2.18 ± 0.4	85.9	1.55 ± 0.3	92.2	1.57 ± 0.5	92.1	5.50 ± 0.8	72.5
Cd	4.88 ± 0.2	75.6	3.916 ± 0.2	80.4	3.831 ± 0.2	80.8	4.904 ± 0.2	75.5
Cu	5.122 ± 0.3	74.4	4.207 ± 0.5	79.0	4.064 ± 0.5	79.7	4.196 ± 0.6	79.05
Fe	6.2 ± 0.5	69.0	5.90 ± 0.3	70.0	5.5 ± 0.7	72.0	6.0 ± 0.2	65.0
Zn	0.552 ± 0.1	97.2	4.91 ± 0.1	75.4	4.80 ± 0.2	76.0	5.20 ± 0.0	74

ANS - Arachis Nut Shells

MSP - Moringa Seed Pods

Table 4: Effect of different particle size of adsorbent with ANS as adsorbent

Initial metal concentration 20 (mg/L)	Final metal concentration (mg/L) with different particle size					
	1mm	%Removal	2mm	%Removal	4mm	%Removal
Pb	3.81 ± 0.4	80.9	4.05 ± 0.5	79.7	4.16 ± 0.5	79.2
Cd	3.70 ± 0.3	81.5	3.71 ± 0.2	81.4	3.73 ± 0.03	81.3
Cu	3.75 ± 1.3	81.2	3.80 ± 0.6	81.0	3.95 ± 0.6	80.2
Fe	4.024 ± 0.4	79.9	4.112 ± 0.2	79.4	4.238 ± 0.03	78.8
Zn	3.41 ± 0.5	82.9	3.89 ± 0.2	80.5	3.91 ± 0.5	80.4

Table 5: Effect of different particle size of adsorbent with MSP as adsorbent

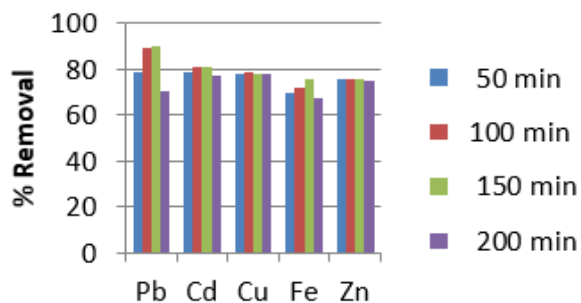
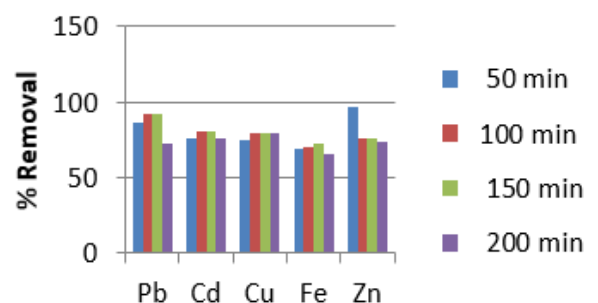
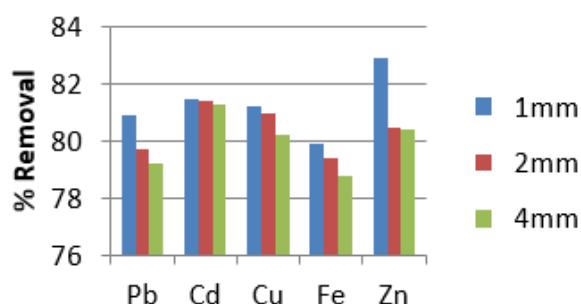
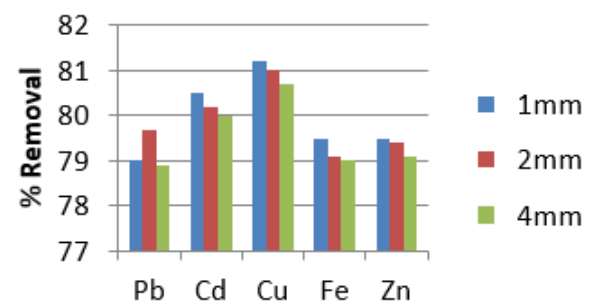
Initial metal concentration 20 (mg/L)	Final metal concentration (mg/L) with different particle size					
	1mm	%Removal	2mm	%Removal	4mm	%Removal
Pb	4.19 ± 0.5	79.0	4.06 ± 0.3	79.7	4.21 ± 0.1	78.9
Cd	3.90 ± 0.2	80.5	3.96 ± 0.2	80.2	3.99 ± 0.4	80.0
Cu	3.75 ± 0.2	81.2	3.79 ± 0.5	81.0	3.85 ± 0.9	80.7
Fe	4.09 ± 0.5	79.5	4.18 ± 0.1	79.1	4.20 ± 0.1	79.0
Zn	4.10 ± 0.5	79.5	4.12 ± 0.2	79.4	4.17 ± 0.1	79.1

Table 6: Effect of different dose of adsorbent with ANS as adsorbent

Initial metal concentration 20 (mg/L)	Final metal concentration (mg/L) with different doses					
	0.5 gm	%Removal	1.0 gm	%Removal	2.0 gm	%Removal
Pb	3.35 ± 0.8	83.2	2.8 ± 0.4	86.0	2.0 ± 0.1	90.0
Cd	3.890 ± 0.0	80.5	3.766 ± 0.3	81.2	3.72 ± 0.4	81.4
Cu	3.85 ± 0.05	80.7	3.79 ± 0.3	81.0	3.70 ± 0.4	81.5
Fe	3.894 ± 1.3	80.5	3.901 ± 1.1	80.5	4.018 ± 0.7	79.9
Zn	4.54 ± 0.2	77.3	4.17 ± 0.3	79.1	3.98 ± 0.3	80.1

Table 7: Effect of different dose of adsorbent with MSP as adsorbent

Initial metal concentration 20 (mg/L)	Final metal concentration (mg/L) with different doses					
	0.5 gm	%Removal	1.0 gm	%Removal	2.0 gm	%Removal
Pb	3.99 ± 0.1	80.0	3.15 ± 0.3	84.2	2.07 ± 0.1	89.6
Cd	3.23 ± 0.2	83.8	3.01 ± 0.2	84.9	2.13 ± 0.1	89.3
Cu	3.179 ± 0.6	84.1	2.730 ± 0.6	86.3	0.029 ± 12.9	99.9
Fe	3.78 ± 0.3	81.1	3.11 ± 0.1	84.4	2.09 ± 0.2	89.5
Zn	4.211 ± 0.2	78.9	4.127 ± 0.8	79.4	2.853 ± 0.7	85.7

%Removal of metal ions with variable contact time using ANS**Fig. 1: Removal of metal ions with variable contact time using ANS****% Removal of metal ions with variable contact time using MSP****Fig. 2: Removal of metal ions with variable contact time using MSP****% Removal of metal ions with variable particle size of ANS****Fig. 3: Removal of metal ions with variable particle size of ANS****% Removal of metal ions with variable particle size of MSP****Fig. 4: Removal of metal ions with variable particle size of MSP**

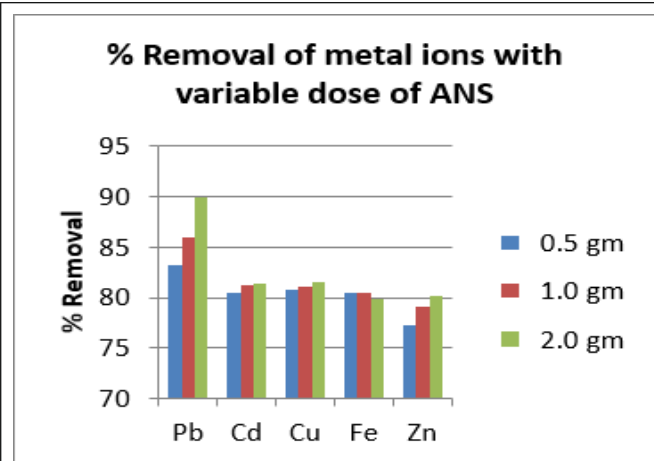


Fig. 5: Removal of metal ions with variable dose of ANS

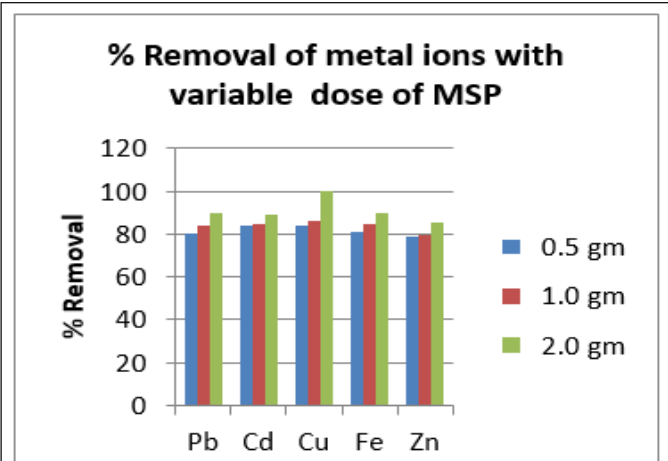


Fig. 6: Removal of metal ions with variable dose of MSP

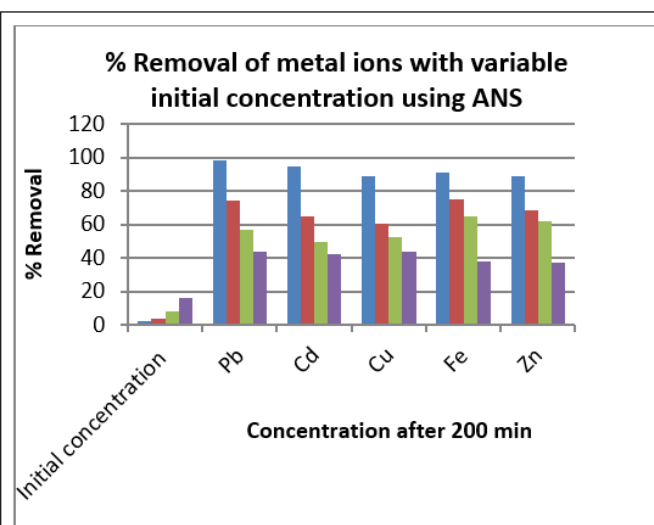


Fig. 7: Removal of metal ions with variable initial concentration using ANS as adsorbent

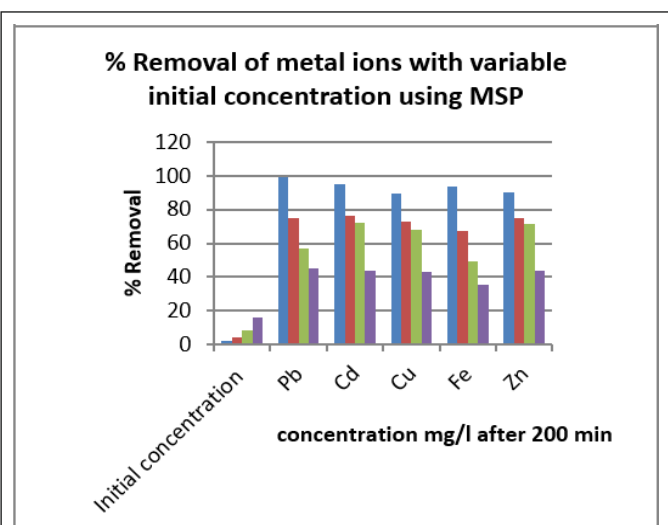


Fig. 8: Removal of metal ions with variable initial concentration using MSP as adsorbent

CONCLUSION:

Moringa oleifera seed pods and *Arachis hypogaea* nut shells were used to successfully remove selected heavy metals from water samples. This work explored the possibility of adding value to waste material by recycling and reusing for purification of contaminated water. The initial metal concentration, sorbent dose and particle size were found to affect the sorption process. The developed method was found to be simple, cheap, environmental friendly, and does not need trained personnel to use it. Hence, it can be a remedial solution for water scarcity in rural areas where there are no resources to obtain the expensive conventional techniques.

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